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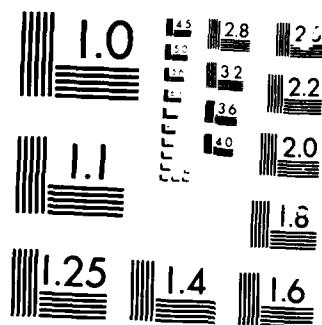
REACTIONS OF LASER-GENERATED FREE RADICALS AT  
SEMICONDUCTOR SURFACES(U) MASSACHUSETTS INST OF TECH  
CAMBRIDGE DEPT OF CHEMISTRY J I STEINFELD 25 NOV 85  
AFOSR-86-0103 AFOSR-83-0007 F/G 7/4

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## REPORT DOCUMENTATION PAGE

DEC

3 1985 D INSTRUCTIONS  
BEFORE COMPLETING FORM

(2)

1. REPORT NUMBER

AFOSR-TR- 86-0103

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

TITLE (and Subtitle)

Reactions of Laser-Generated Free Radicals at  
Semiconductor Surfaces5. TYPE OF REPORT & PERIOD COVERED  
Final; 10/1/82 - 9/30/85

6. PERFORMING ORG. REPORT NUMBER

AUTHOR(s)

J.I. Steinfeld

8. CONTRACT OR GRANT NUMBER(s)

AFOSR-83-0007

PERFORMING ORGANIZATION NAME AND ADDRESS

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 0213910. PROGRAM ELEMENT, PROJECT, TASK  
AREA & WORK UNIT NUMBERS

61102F 2303/B1

CONTROLLING OFFICE NAME AND ADDRESS

Air Force Office of Scientific Research /NC  
Bolling Air Force Base  
Washington, DC 20332

12. REPORT DATE

11/25/85

13. NUMBER OF PAGES

6

14. MONITORING AGENCY NAME &amp; ADDRESS (if different from Controlling Office)

Same

15. SECURITY CLASS. (of this report)

UNCLASSIFIED

15a. DECLASSIFICATION DOWNGRADING  
SCHEDULE N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of abstract entered in Block 20, if different from Report)

Same

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary, and identify by block number)

-surface chemistry	laser-induced fluorescence
semiconductors	multiple-photon excitation
fluorocarbons	chemisorption
silicon	laser photochemistry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Reactions of laser-generated free radicals at semiconductor surfaces have been investigated by photoelectron spectroscopy of adsorbed surface layers and by laser-induced fluorescence detection of the gas-phase species. Systems investigated include dissociative chemisorption of  $\text{XeF}_2$  and  $\text{CF}_3$  on  $\text{Si}(111)$ , IR multiple-photon dissociation of alkylsilanes and characterization of  $\text{SiH}_2$ . Theoretical calculations of spectroscopic, structural, and thermodynamic properties of reactive free-radical intermediates have also been undertaken.

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FINAL REPORT

to the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

on

Grant No. AFOSR-83-0007

"Reactions of Laser-Generated Free Radicals  
at Semiconductor Surfaces"

by

Jeffrey I. Steinfeld  
Professor of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

(25 November 1985)

Approved for Release by NSA on 09-11-2013 pursuant to E.O. 13526

There is considerable interest in gaining an understanding of the chemical mechanisms involving reactive gas-phase species at semiconductor surfaces. These reactions may lead to either etching (transport of material from the surface as volatile products) or deposition of thin films on the surface. Both of these processes are essential steps in the fabrication of microelectronic devices.

The current state-of-the-art in etching and deposition is the RF plasma technique. While this technique is effective, its fundamental mechanisms are still poorly understood, which makes it difficult to extend the technique beyond its present limits, e.g., to submicron definition (VLSI) or to new materials. We have been carrying out an interrelated series of investigations addressing these problems, viz.: (1) detailed analysis of surface-adsorbed species and desorbed products in etching reactions of semiconductors, principally silicon; (2) optical probes for reactive gas-phase species; (3) improved understanding of plasma processes; and (4) generation of surface-active species by infrared multiple-photon dissociation (IRMPD).

An ultra-high vacuum apparatus for surface analysis measurements, incorporating a quadrupole mass spectrometer, UPS, XPS, LEED, Auger, and optical access for infrared radiation has been completed. Initial experiments have been directed toward characterizing the interaction of free fluorine with single-crystal Si(111)7x7, using XeF<sub>2</sub> as the fluorine source. A product with (m/e) = 85, attributed to either SiF<sub>3</sub> or SiF<sub>4</sub>, desorbes in the neighborhood of 250°C, while SiF<sub>2</sub> begins to appear as the more fluorinated product tails off and peaks at ~400°C. At higher XeF<sub>2</sub> doses, the yield of SiF<sub>3</sub> (SiF<sub>4</sub>) increases dramatically, but that of SiF<sub>2</sub> is essentially constant. These results suggest the presence of at least two distinct sites on this surface, one leading to SiF<sub>4</sub> formation and the other producing SiF<sub>2</sub>. X-ray photoelectron spectroscopy

of the F(1s) level have shown that only one type of fluorine is observed on a stable overlayer in this system. At very high dosage levels, additional features appear in the F(1s) and Si(2p) XPS line, and SiF<sub>4</sub> [*m/e* = 104] is observed as a desorption product. These and related results can be explained by migration of F atoms in the lattice, either vertically from bulk to surface sites or laterally from one binding site to another.

Experiments are currently under way using fluorocarbon etchants (C<sub>2</sub>F<sub>6</sub>, CF<sub>3</sub>I). A very slow spontaneous decomposition occurs with CF<sub>3</sub>I ( $\alpha_r \approx 10^{-7}$ ), producing adsorbed CF<sub>2</sub> and CF<sub>3</sub> moieties and leading to desorption of SiF<sub>2</sub> and SiF<sub>3</sub> products. Dissociation of the C<sub>2</sub>F<sub>6</sub> by IRMPD results in chemisorbed C and F on the surface; from the XPS peak positions, it appears that most of the F atoms are transferred from C to Si in the adsorption process. The presence of coadsorbed adventitious hydrocarbons blocks the F atom transfer process. (Joyce *et al.*, 1984; Roop *et al.*, 1985).

An apparatus has been completed in which reactive species (CF<sub>2</sub>, SiF<sub>2</sub>, SiH<sub>2</sub>, CF<sub>3</sub>, etc.) may be produced by either infrared multiple-photon dissociation or u.v. photolysis, or generated in a d.c. discharge. Laser-induced fluorescence is used for quantitative detection of these species in the gas phase and following interaction with surfaces. Initial measurements using this technique have concentrated on the reactions of CF<sub>2</sub>, detected via its  $\tilde{A}-\tilde{X}$  transition at 261 nm, with Si and SiO<sub>2</sub>. A simple reaction-diffusion model predicts the radical concentration *n*(*z*) to depend on vertical distance from the surface, *z*, in a simple linear fashion, from which the net surface reaction probability  $\alpha_r$  can be determined. The data for CF<sub>2</sub> yield values of  $\alpha_r = (0.021 \pm 0.007)$  for Si(111),  $\alpha_r = (3.5 \pm 0.4) \times 10^{-3}$  for SiO<sub>2</sub>.

SiH<sub>2</sub> has been detected (via its  $\tilde{A}^1B_1 - \tilde{X}^1A_1$  transition) following IRMPD of organosilanes. The radiative lifetimes of rovibronic levels of the  $\tilde{A}$  state

show a wide variation, which is attributed to mixing with the  $\tilde{a}^3B_1$  state (Thoman and Steinfeld). Analysis of these perturbations is presently under way.

Several theoretical investigations related to the experimental program have also been carried out. An analytical model has been developed for the electric potentials of a plasma and both electrodes in a diode type RF discharge. This model gives better agreement with experiment than the previous model of Koenig, and reproduces the numerical calculations of Keller and Pennebaker (Suzuki et al.). Also, since the spectroscopic properties of many of the reactive species of interest are not well known, ab initio calculations of these properties have been undertaken. Structural, spectroscopic, and thermochemical properties have been calculated at the 3-21G/SCF level for trifluoromethoxy, -methyltrioxy, and related free-radical species (Francisco et al., 1985; Francisco, 1985; Francisco and Williams, 1985).

Our principal technique for generating these free radicals is infrared multiple-photon dissociation (IRMPD). Since our understanding of the IRMPD process is far from complete, we have undertaken a number of studies designed to elucidate the details of this process. These have included master-equation modelling of IRMPD in chloroethane (Francisco et al., 1983) and the use of laser-induced fluorescence to probe vibrational levels of thiophosgene in a molecular beam following CO<sub>2</sub> laser excitation (Brenner et al., 1983). More recently, we have been using CARS to probe CO<sub>2</sub>-laser-excited molecules, including chloroethane. A retrospective of our work on infrared laser photochemistry has been prepared for publication in an edited series (Francisco and Steinfeld, in press).

LIST OF PUBLICATIONS

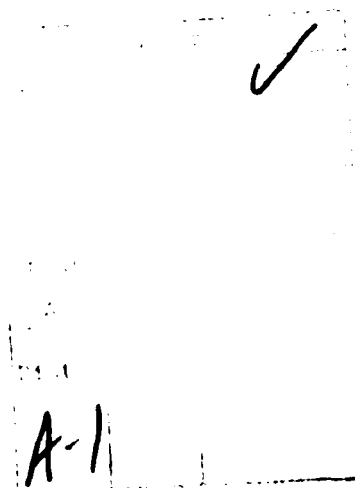
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